PATENT SPECIFICATION 1,084,696

DRAWINGS ATTACHED.

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1,084,696

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COMPLETE SPECIFICATION.

Method for Preparing Thin Films of Rare Earth Chalcogenides.

We, INTERNATIONAL BUSINESS MACHINES CORPORATION, A Corporation organized and existing under the laws of the State of New York in the United States of America, of Armonk, New York 10504, United States of America (assignees of
America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

The invention relates to the preparation of thin films of rare earth chalcogenides.

By rare earth chalcogenides is meant compounds of rare earth elements with ogygen, sulphur, selenium and tellurium. The optical, electric, and magnetic properties of thin films of rare earth chalcogenides are attracting increasing interest. These properties are influenced by the composition of the film and on the impurities present in the film. It is, therefore, important that these films be prepared with the desired composition.

Rare earth elements such as europium are very strongly reactive metals so that the preparation of pure rare earth chalcogenides has presented some difficulty. Since the exothermic reaction takes place quite violently at the high temperatures, 600 to 700°C, required by prior at methods, contamination of the film is difficult to avoid.

The present invention provides a method for preparing a thin film of rare earth chalcogenide as defined herein comprising evaporating a film of a rare earth metal onto an inert substrate in a chamber under vacuum, and then introducing a hydrogen chalcogenide gas namely H_2O, H_2S, H_2Se or H_2Te to react with the metal film whereby the rare earth chalcogenide film is formed on the substrate.

The invention will now be described by way of example with reference to the accompanying drawing which shows an apparatus for preparing thin films of rare earth chalcogenides.

The drawing shows a vacuum chamber 10 is which the rare earth chalcogenides film is prepared. The chamber is preferably of glass. A vacuum pump 16 is connected to the exhaust tube 18 of the chamber through a valve 17. Initially a rare earth metal 11, such as europium is placed in a crucible 12 of high temperature melting material such as tantalum. The chamber is then evacuated to a pressure lower than 10^{-8} Torr. The chamber can be well baked (by heating means not shown) to assist in producing this ultra high vacuum. The crucible 12 is then heated. In the drawing a cathode ring 13, the electrodes of which are connected to the current source 14, surrounds the crucible. Alternatively, inductive or other heating methods could be used.

A substrate 15, on which the rare earth film is depositied is positioned above the crucible. The substrate must be inert chemically and in particular must not react with the rare earth metal at room temperature. Suitable substrates are glass, quartz, sapphire, or magnesium oxide. The rare earth metal film deposited on the substrate can be up to 100μ thick. A very pure rare earth metal film is thus obtained.

When the rare earth metal film has been formed, the desired chalcogenide film is formed by introducing the apropriate gas, that is one of the following: hydrogen sulphide, hydrogen selenide, hydrogen telluride

and water vapour into the chamber through tube 19, washing bottle 20, tube 21 and valve 22. The pressure of the gas is approximately atmospheric. When preparing the oxide film the pressure in the chamber is preferably reduced to below atmospheric to avoid the formation of unwanted oxides for example when EuO film is prepared the unwanted oxide is Eu_2O_3.

The gas reacts with the pure rare earth metal on the substrate at room temperature to form the desired rare earth chalcogenide. The reaction begins at the surface of the metal film and slowly continues throughout the entire layer. The result is a thin film of rare earth chalcogenides of extraordinary chemical purity. For example, when europium is deposited on the substrate and hydrogen sulphide introduced into the chamber a film of europium sulphide is formed. The reaction can be expressed as follows:

$$Eu + H_2S \longrightarrow EuS + H_2.$$

Contamination is avoided by the reaction taking place at room temperature. Higher temperatures would accelerate the reaction; but contamination with impurities from the crucible material or the apparatus walls would then be difficult to avoid. The speed of the reaction at room temperature can be controlled by varying the gas pressure. The materials of the chamber, substrate and crucible are chosen so that they do not react with the rare earth metal.

Doped rare earth chalcogenide films can also be prepared if particular properties are required. For example, if a small quantity of gadolinium is deposited along with europium and the sulphide of both metals formed the conductivity of the film is increased and Curie temperature is raised. Thus both the conductivity type, the electrical conductivity and the magnetic properties of the films can be varied by using different doping materials. The sulphides, tellurides, selenides or oxides of univalent alkali metals or trivalent rare earths can be used as doping materials.

EuSe and GdSe, as well as EuS and GdS, will form alloys of any desired proportion. Europium and gadolinium are magnetically equivalent since their 4f electrons have the same ground state. The electrical conductivity of such an alloy can be continuously varied over a range of 12 decimal powers from the insulator to the metal state.

Our United Kingdom Patent No. 1,033,857 claims a single crystal film of europium II oxide, sulphide or selenide.

WHAT WE CLAIM IS:—

1. A method for preparing a thin film of a rare earth chalcogenide as defined herein comprising evaporating film of a rare earth metal on to an inert substrate in a chamber under vacuum, and then introducing a hydrogen chalcogenide gas to react with the metal film whereby the rare earth chalcogenide film is formed on the substrate.

2. A method as claimed in claim 1, in which the gas is hydrogen sulphide.

3. A method as claimed in claim 1, in which the gas is hydrogen selenide.

4. A method as claimed in claim 1, in which the gas is hydrogen telluride.

5. A method as claimed in claim 1, in which the gas is water vapour.

6. A method as claimed in any one of the preceding claims, in which the rare earth metal is europium.

7. A method as claimed in any one of the preceding claims, in which the thickness of the metal film is 100 μ.

8. A method as claimed in any one of the preceding claims, in which the substrate is of glass, quartz, sapphire or magnesium oxide.

9. A method as claimed in any one of the preceding claims, in which the pressure in the chamber is less than 10^{-5} Torr during evaporation and approximately atmospheric during the reaction.

10. A method as claimed in any one of the preceding claims, in which the chamber is approximately at room temperature during the reaction.

11. A method as claimed in any one of the preceding claims, including providing in the chamber an inert crucible of high temperature melting material containing a source of rare earth metal.

12. A method as claimed in claim 11, in which the crucible is of tantalum.

13. A method as claimed in any one of the preceding claims including simultaneously evaporating a doping material with the rare earth metal onto the subtrate.

14. A method as claimed in claim 13, in which the doping material is a trivalent rare earth metal.

15. A method as claimed in claim 14, in which the trivalent rare earth metal is gadolinium.

16. A method as claimed in claim 13, in which the doping material is an alkali metal.

17. A method for preparing a thin film of a rare earth metal chalcogenide as claimed in any one of the preceding claims substantially as described herein.

18. A rare earth chalcogenide film when prepared by a method claimed in any preceding claim.

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1 SHEET *This drawing is a reproduction of the Original on a reduced scale*